

# THE EFFECTS OF $T_1$ AND NOE CONSIDERATIONS IN QUANTITATIVE APPLICATIONS OF CARBON-13 NMR TO THE ANALYSIS OF COMPLEX HYDROCARBON MIXTURES

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## I. Introduction

Since the signal intensities of a nuclear magnetic resonance spectrum are dependent upon the number of given nuclei present in a compound, nuclear magnetic resonance can be a strong analytical tool for quantifying the amounts of material present in a sample. In many compounds of interest which contain carbon, carbon-13 magnetic resonance (cmr) spectra are of particular value as an analytical tool since the spectra can be void of multiplet structure due to  $^{13}\text{C}$ - $^{13}\text{C}$  splittings (if carbon is in natural abundance only) and can be void of multiplet structure due to  $^1\text{H}$ - $^{13}\text{C}$  splittings (if noise-modulated proton decoupling techniques are used). Moreover, a range of chemical shifts of over 200 ppm for common functional groups assist greatly in resolving individual peaks in any given spectrum (1). Thus under such experimental conditions, each  $^{13}\text{C}$  nuclear environment is represented by a single  $^{13}\text{C}$  resonance. In complex mixtures of hydrocarbons resulting from coal liquification, these qualities of cmr make  $^{13}\text{C}$  spectra particularly useful. Such coal mixtures can contain hundreds of compounds, and may be quite viscous. In such mixtures,  $^{13}\text{C}$  spectra have been used by various workers to quantify the amount of a given compound, as well as to quantify the amount of aromaticity in given coal derivative samples (2-4).

Nevertheless, there are some problems attendant with the  $^{13}\text{C}$  nmr technique and the usefulness of the  $^{13}\text{C}$  signal intensity as a quantifiable parameter. To begin with,  $^{13}\text{C}$  nuclei in natural abundance amount to only about 1.1%. In complex mixtures of multiple compounds, signal sensitivity therefore becomes a problem. Fourier transform methods of data acquisition with repeated pulse sequences and data storage for signal averaging, has somewhat overcome such complications (4). However, such Fourier techniques themselves lead to other problems. To ensure that the time necessary to store sufficient transients is not inordinately long, it is desirable to repeat the pulse sequence as rapidly as possible. Nevertheless, the delay time between successive pulse sequences (individual transients) is dependent upon the spin-lattice relaxation times ( $T_1$ ) of the  $^{13}\text{C}$  system. If the next pulse sequence is begun before any given  $^{13}\text{C}$  signal has had an opportunity to relax to its thermal equilibrium value, saturation effects occur, and the resultant  $^{13}\text{C}$  signal intensity is not maximized. For hydrocarbon systems which contain a wide variety of carbon-13 relaxation times from fairly short (2 sec) to fairly long (200 sec), this creates a problem. Reasonable delay times of 1-10 seconds between successive  $90^\circ$  pulses would most likely saturate the  $^{13}\text{C}$  signals with long relaxation times (200 sec) so that less than 10% of the possible signal would be observed. In contrast, delay times of 1-10 seconds with  $90^\circ$  pulses could permit nearly 90% of the signals to be observed if the relaxation times were short (2 sec). Under such variable saturation effects, the  $^{13}\text{C}$  signal intensities would be difficult to relate to quantifiable results (4).

For hydrocarbon systems which result from coal derivatives, such wide variations in relaxation times are a reality. Spin-lattice relaxation times in acenaphthene have been reported to vary from 3.1 seconds for the  $^{13}\text{C}$  nuclei with two protons attached, to about 150 seconds (5a,5b,5c) at the internal bridgehead carbon. A similar range of the spin-lattice relaxation times for the protonated and non-protonated carbons in pyrene has been observed. Since delay times of  $5T_1$  are necessary to ensure complete relaxation following a  $90^\circ$  or  $180^\circ$  pulse (6), some other method must be found for taking  $^{13}\text{C}$  signal intensities in

hydrocarbon systems with long relaxation times. Repeated pulse sequences (1,000 to 10,000 transients) with delay times of 1,000 seconds ( $5T_1$ ) become prohibitively long to run (for example, 10,000 transients with delay times of 1,000 sec between transients would take 116 days per spectrum).

Another problem inherent in the proton-decoupled  $^{13}\text{C}$  spectra relates to the Nuclear Overhauser Effect (NOE) experienced by the  $^{13}\text{C}$  signals when the coupled  $^1\text{H}$  nuclei are doubly irradiated. It has been observed that  $^{13}\text{C}$  intensities are enhanced when coupled  $^1\text{H}$  signals are irradiated by a saturating second frequency. The value of the NOE is determined by the ratio of  $S \approx S_0$ . (The  $^{13}\text{C}$  signal intensity after the proton decoupler has been on long enough to establish equilibrium is  $S \approx S_0$  is the signal intensity without proton decoupling) (7). Depending upon whether a given nucleus is dominated by dipole-dipole relaxation, or by other relaxation mechanisms, the value of NOE can vary from 3 to 1, respectively (8,9). In the hydrocarbon systems of coal derivatives, it appears that the NOE factors can vary over the maximum ranges (being about 3 if protons are directly attached, and as low as 1-2 if no protons are attached). Hence, variations in NOE enhancements of  $^{13}\text{C}$  signal intensities representing the same number of  $^{13}\text{C}$  nuclei could vary over a magnitude of 1-3 (8). This is hardly acceptable for quantitative studies. Thus, some means of either quickly determining the NOE factors for each  $^{13}\text{C}$  signal must be found, or else some means of eliminating the NOE enhancement must be used.

In an effort to address the preceding problems we have obtained  $T_1$  and NOE values on a number of model compounds (polycyclicaromatic hydroaromatic, and alkylated aromatic hydrocarbons) which are thought to have representative values similar to those found in complex hydrocarbon mixtures. The  $T_1$  and NOE values thus obtained provide valuable information on relaxation processes, range of values expected, and details of molecular motion.

## II. Experimental

The  $T_1$  and NOE data were taken at 25 MHz and 75 MHz on Varian XL-100-15 and SC-300 FT spectrometers, respectively.  $T_1$ 's were obtained by the inversion recovery method (10) while NOE values were obtained by a two point gated decoupling method.

## III. Results and Discussion

We have obtained  $T_1$  and NOE data on naphthalene, tetralin, acenaphthene, pyrene, symmetrical hexahdropyrene, phenanthrene, 1,2,3,4,5,6,7,8, octahydro-phenanthrene, xanthone, and phenyloctane. This group of compounds represent a set of structural types representative of many moieties known to occur in coal derived liquids. In terms of general relaxation considerations the data can be considered, for convenience, in terms of protonated and non-protonated carbons. Protonated carbons are found, within experimental error, to exhibit essentially a full nuclear overhauser effect and the dipolar relaxation mechanism thus is dominant (11). The  $T_1$  values at 25 MHz for all protonated carbons examined fall in the range of 2-11 second. Similar values are observed at 75 MHz. The non-protonated carbons, however, fall in the range 28-240 seconds at 25 MHz with the higher numbers associated with the PAH's where the  $1/r_{CH}^6$  term in the relaxation expression rapidly alternates the efficient carbon-hydrogen intramolecular dipolar relaxation mechanism.

Some very interesting results are observed for the non-protonated carbons at 75 MHz. The  $T_1$  values are shortened considerably indicating significant contributions made by chemical shift anisotropy at high fields. Using the rate expression (11)

$$\frac{1}{T_1} = \frac{1}{T_1^D} + \frac{1}{T_1^{CSA}} + \frac{1}{T_1^O} \quad (1)$$

and assuming that  $1/T_1^O$  approaches zero for the systems in question (which, based on the low and high field data, is justified), one can readily calculate dipolar

contributions of 88, 413, and 127 seconds, to the relaxation rates at C-9,10,C-11, and C-12, respectively by assuming isotropic motion of the molecules. The chemical shift anisotropy term is 88, 73, and 54 seconds, respectively for these carbons. In the case of pyrene the contribution from chemical shift anisotropy is even greater with contribution of 35 and 38 seconds for carbons 11,12,13,14 and 15,16 respectively. Hence, relaxation constraints are much less severe at high fields than those encountered using iron core magnet NMR technology.

Based on the data obtained to date, we estimate that the non-protonated carbons at C-15,16 in pyrene represent the longest  $T_1$  values one would expect to encounter. Using mixtures of these compounds we have varied spectrometer operating conditions in order to arrive at an optimal set of parameters for use on coal derived liquids. Details of the results of these studies at 25 and 75 MHz will be forthcoming.

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9. It should be noted, see Ref. 7 for a complete description, that if the liquid is not in the region of motional narrowing,  

$$\text{i.e., } (\omega_{\alpha\beta}^2 \tau_c^2 \ll 1),$$
the NOE will not be equal to 3 even if the relaxation is totally dipole-dipole dependent (transition probabilities and hence relaxation mechanisms are related to:

$$W_{\alpha\beta} = \gamma^2 H^*_{\text{Loc}}(t) H_{\text{Loc}}(t) \left( \frac{\tau_c^2}{1 + \omega_{\alpha\beta}^2 \tau_c^2} \right)$$

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TABLE I

Relaxation Parameters in Pyrene and Acenaphthene

COMPOUND	POSITION	$T_1$ $\frac{25 \text{ MHz}}{\eta} (\pm 0.2)$		$T_1$ $\frac{75 \text{ MHz}}{\eta} (\pm 0.2)$	
Acenaphthene	1,2	3.1 $\pm$ 0.2	3.0	3.1	1.95
	3,8	5.6 $\pm$ 0.8	2.8	6.0 $\pm$ 0.4	1.85
	4,7	5.6 $\pm$ 0.8	2.8	6.6 $\pm$ 0.5	1.85
	5,6	6.4 $\pm$ 0.9	2.8	6.5 $\pm$ 0.4	1.85
	9,10	87 $\pm$ 10	2.3	44 $\pm$ 2	1.0
	11	208 $\pm$ 30	1.8	62 $\pm$ 7	0.4
	12	128 $\pm$ 10	2.1	38 $\pm$ 3	0.4
Pyrene	1,3,6,8	8.0 $\pm$ 0.4	1.9	4.9 $\pm$ 0.4	2.0
	2,7	6.8 $\pm$ 0.2	1.9	4.5 $\pm$ 0.3	2.0
	4,5,9,10	7.2 $\pm$ 0.8	1.9	5.4 $\pm$ 0.2	2.0
	11,12,13,14	135 $\pm$ 10	1.2	26.2 $\pm$ 1.4	0.51
	15,16	240 $\pm$ 30	0.6	35.1 $\pm$ 3.5	0.17